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# Hyperconjugative Effects on Carbon–Carbon Bond Lengths in Molecular Mechanics (MM4)\*

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## ABSTRACT

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The hyperconjugative result of bond stretching in alkenes has been studied with MM4. A low-temperature crystallographic study of 1,2-diaryllindane[a]indane has been carried out, together with *ab initio* (MP2/6-31G\*) calculations on model systems. The results are well reproduced with a force field designed to explicitly include hyperconjugation (MM4), and they show beyond doubt that hyperconjugative bond elongations exist both in theory and by experiment.

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## Introduction

The objective of molecular mechanics is to develop a model that accurately portrays structural and related features of molecules.<sup>1</sup> In the first approximation, a force field that is essentially harmonic and diagonal is used to describe a

molecule. Better approximations consist in part of adding anharmonic terms to the potential functions and of adding explicit off-diagonal quantities in formulating the force constant matrix. For a molecular mechanics force field to be of practical value, the various terms must be transferable, and hence it is important to include only those anharmonic terms and off-diagonal elements that can be clearly shown to exert a significant transferable effect. The MM4 force field is a current example of a force field which contains several of the latter types of terms.<sup>1,2</sup>

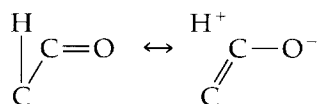
\*This article includes Supplementary Material available from the authors upon request.

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Molecular mechanics is a powerful tool for teaching us what we do or do not understand about chemistry. If we can correctly calculate a structure using molecular mechanics, all is fine. If we cannot, then our computational model is deficient. This means that there is something that we do not know about chemistry, or at least that we have not properly taken into account in developing the force field.

Hyperconjugation, if it exists at all, is a relatively subtle effect<sup>3</sup> which can be neglected to the first approximation in calculations on molecular structures (neutral, closed-shell ground states). However, if one wants to calculate accurate structures, then this is clearly something that needs to be considered. Earlier, we examined the question of what happens to bond lengths when they are in the  $\alpha$ - $\beta$  position to a carbonyl group, as a function of torsion angle.<sup>4</sup> *Ab initio* calculations at the 4-21G level showed that, in the case of acetaldehyde, for example, the C—H bond on the methyl group lengthened by about 0.006 Å if it were oriented perpendicular to the carbonyl plane relative to when it was in the carbonyl plane. Later calculations with larger basis sets and electron correlation show substantially the same results.<sup>5</sup>

The hyperconjugation involved in this example can be expressed in terms of the following valence bond structures:



When the C—H bond is perpendicular to the carbonyl plane, there is maximum overlap between the C—H bond  $\sigma$  orbital (the  $p$  component) and the  $\pi^*$  orbital of the carbonyl carbon. In this geometry, as the C—H bond donates electron density to the  $\pi^*$  orbital, it becomes longer, and the positive charge on the hydrogen increases, as indicated by the resonance structure at the right. The effect is minimal when the hydrogen is in the carbonyl plane, and the orbitals involved here are orthogonal.

For the C—H bond of the methyl group in acetaldehyde, a bond 90° out of plane was calculated to be longer than one in the plane by 0.006 Å. The corresponding change for a C—C bond was calculated to be much larger, 0.016 Å. The sizes of these bond length variations are small enough to ignore to a first approximation. The latter value, however, is certainly within the detectable range of good experiments.

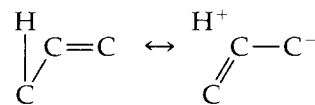
The bond stretching of the C—H (or C—C) bond can be represented approximately by eq. (1).

$$\Delta l = k(1 - \cos 2\omega) \quad (1)$$

where  $\Delta l$  is the bond length change,  $k$  is a constant for a given bond, and  $\omega$  is the dihedral angle about the C—C—C—O bond. [We refer to this as a torsion-stretch type (2) to differentiate it from type (1), where the bond that stretches is the one about which the torsion occurs.] In MM3,<sup>‡</sup> the constant ( $k$ ) has numerical values of 0.0025 Å for the C—H bond in the carbonyl compound and 0.0080 Å for the C—C bond, and the maximum change in bond length from this effect is  $2k$ . The  $\Delta l$  correction in MM3 was applied not to  $l$ , but to  $l_0$ , and the usual energy minimization was then carried out. This approach has the disadvantage that  $\Delta l$  has to be recomputed at every iteration, and the procedure is slowly convergent. The procedure was changed in MM4, and now one computes a torsion-stretch matrix element that is added directly into the force-constant matrix. Here the element is the second derivative of the torsion-stretch energy given by the following relationship:

$$E_{\text{TS2}} = -0.5(l - l_0)11.995(K_{V1}(1 + \cos \omega) + K_{V2}(1 - \cos 2\omega)) \quad (2)$$

The carbonyl group involved in the preceding hyperconjugation is a relatively special case, because the oxygen is highly electronegative and the electrons are much stabilized by occupying orbitals to which the oxygen is a significant contributor. However, it is clear that one can write similar resonance forms when the double bond involves only carbon, as in propene. One might anticipate that the effect would be similar in this case, but smaller than in the carbonyl example.



<sup>‡</sup> The MM3 program is available to all users from Tripos Associates, 1699 South Hanley Road, St. Louis, MO 63144; and to academic users only from the Quantum Chemistry Program Exchange, University of Indiana, Bloomington, IN 47405. The current version is available to run on most types of computers, and interested parties should contact one of the distributors directly. It is intended, similarly, to make the MM4 program available in due course.

This effect, in the case of alkenes and related aromatic rings, has been previously discussed in the literature, and some long bonds which have been found experimentally have had their unusual lengths attributed to this kind of effect.<sup>6,8</sup> It is, however, frequently stated in the literature<sup>3,7</sup> that no convincing experimental evidence for the effect of hyperconjugation on the lengthening or shortening of bonds has ever been obtained (for neutral closed shell molecules), but observed changes in nuclear magnetic resonance (NMR)<sup>7</sup> coupling constants have been interpreted as indicating that such hyperconjugation does occur. Most of the earlier discussion on the reality of hyperconjugation is directed at the difference between a C—C bond and a C—H bond in terms of this effect.<sup>11</sup> It might be, however, that the difference in the effect that hyperconjugation has on these two bonds is small relative to the absolute magnitude of the effect. The detection of this effect experimentally presents some practical difficulties. If one measures a bond length, the effect is detectable only if the bond length change can be determined relative to the case in which the effect did not occur. How does one determine the bond lengths in the latter case?

In the present work we have done several things.<sup>†</sup> First, we have carried out some *ab initio* calculations to indicate the approximate magnitude of the effect in the alkene case, to compare it with the carbonyl case. (Radom<sup>11</sup> has given a summary of evidence for hyperconjugation in many ionic and heteroatom systems but did not discuss this kind of situation.) Second, we have summarized a list of compounds previously described in the literature as having long bonds attributable to

<sup>‡</sup> A summary of earlier literature is given in ref. 6.

<sup>†</sup> The usual argument is as follows: If one examines the above resonance form, one sees a proton in the valence bond picture at the right. If the compound in question were 1-butene instead of propene, then one would have an analogous resonance form at the right, but the H<sup>+</sup> would be replaced by a CH<sub>3</sub><sup>+</sup>. The CH<sub>3</sub><sup>+</sup> ion is known to be highly unstable, so it has been argued that that kind of resonance form will not contribute much to the overall structure. On the other hand, H<sup>+</sup> is a more acceptable species, and the corresponding resonance form could be much more important. There is a logical problem with this argument in that H<sup>+</sup> is not particularly stable. The stable species which we meet with in everyday life is really H<sub>3</sub>O<sup>+</sup>. The H<sup>+</sup> in that case is greatly stabilized by solvation. Thus the usual argument that hyperconjugation from a C—C bond can be neglected relative to one from a C—H bond is suspect.

<sup>†</sup> A summary of this work was presented at the 207th Meeting of the American Chemical Society, San Diego, April 1994. N. L. Allinger, *Recent Advances in Molecular Mechanics*, abstract 179.

this effect (Fig. 1).<sup>#</sup> Third, we carried out MM4 calculations on this group of compounds (with hyperconjugation ignored) and noted the bond length errors. Next we devised a molecular mechanics representation of this effect based on the *ab initio* calculations and carried out MM4 calculations on this same group of compounds, including hyperconjugation. The MM4 calculations, with and without hyperconjugation, may then be compared with experiment. Finally, since the effect is relatively small, we have carefully reexamined a particular case (compound 1, Fig. 1, Table I) experimentally by X-ray crystallography at low temperature.

*Ab initio* calculations were carried out (at the MP2/6-31G\* level\*\*) on propene and on 1-butene to ascertain the amount of lengthening to be expected for C—H and C—C bonds as a function of the torsion angle. The C—H bond length difference, relative to the hydrogen oriented 180° from the double bond, increased smoothly by 0.0030 Å as the dihedral angle was reduced to 90°, but then instead of decreasing back to essentially zero at 0°, it went down to 0.0014 Å at 30° and up slightly to 0.0015 Å at 0°. We decided not to implement this small variation for the C—H bond as the maximum error relative to the average value is only 0.0015 Å. For the C—C bond, the variation in length is larger and ranges from zero at 0° up to 0.0078 Å at 90° and back down to 0.0024 Å at 180°. We chose to reproduce this behavior with a simple two-term cosine function [eq. (2)]. The MM4 relative C—C bond length in 1-butene is increased by 0.0077 Å from 0° to 90° and then reduced to 0.0027 Å at 180°. Thus the overall effect here is similar to that observed with the carbonyl compounds, but only about half as large, in agreement with expectations. It is also noted that the total range of stretching is roughly twice as much for a C—C bond as for a C—H bond, similar to what was

<sup>#</sup> That the bond lengths in compounds of this type tend to be unusually long has been appreciated for a long time, as has the general idea that molecular mechanics might be useful for studying such systematic phenomena (ref. 10).

\*\* It was also ascertained that this bond stretching is not highly dependent on the basis set size, or the inclusion of electron correlation in the calculation, by examining the methyl group C—H bond lengths in the ground state conformation of propene. The out-of-plane C—H is longer by the following amounts (basis set): 0.0028 Å (STO-3G); 0.0037 Å (HF/3-21G); 0.0041 Å (HF/6-31G\*); 0.0030 Å (MP2/6-31G\*). Similar but larger differences were generally found for acetone: 0.0015 Å (STO-3G); 0.0049 Å (3-21G); 0.0060 Å (HF/6-31G\*); 0.0047 Å (MP2/6-31G\*). Gaussian92 was used for these calculations (ref. 12).

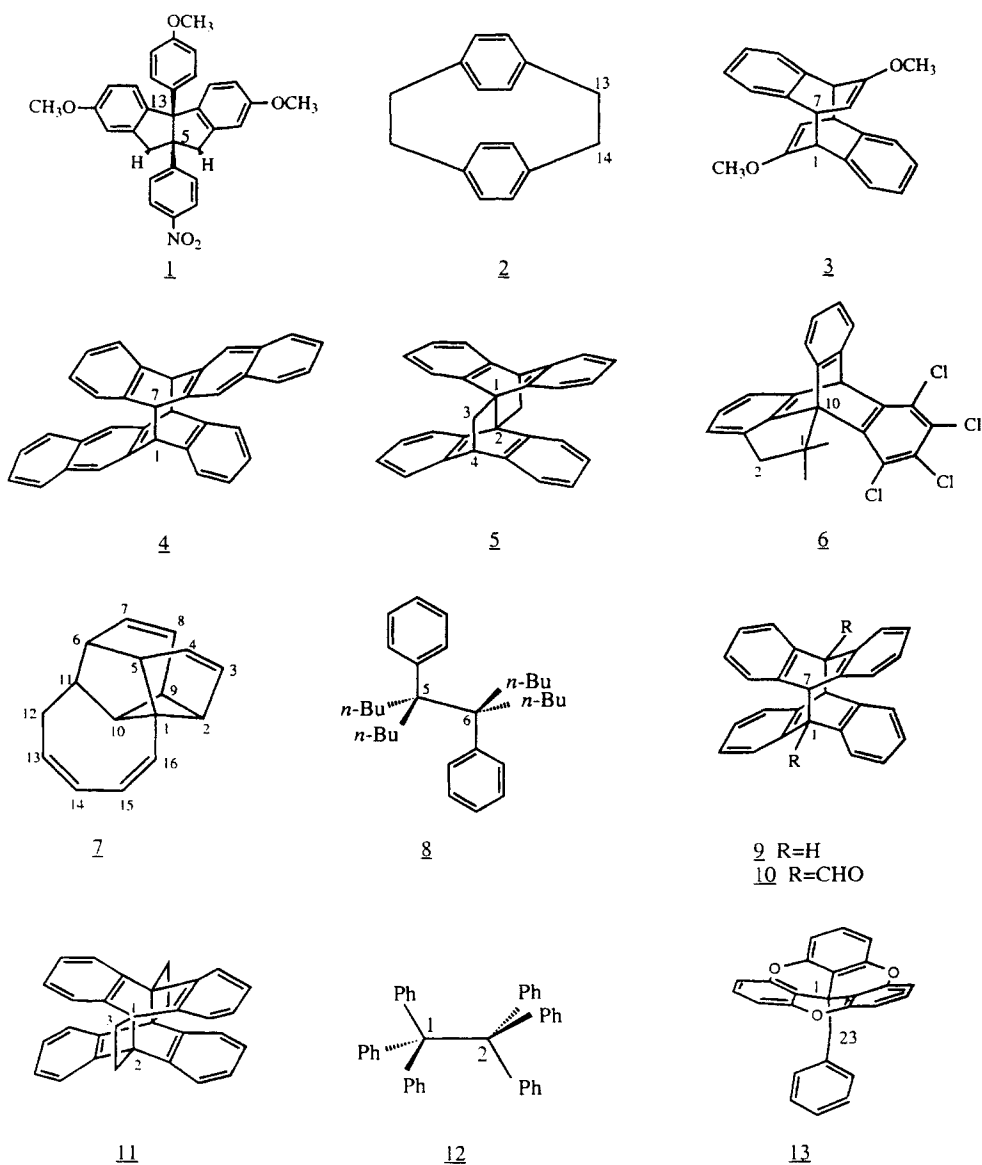


FIGURE 1. Compounds showing long C—C bonds.

found with ketones<sup>4</sup> (contrary to the assumptions made in earlier arguments [see footnote §]).

An examination of the population analysis for propene showed that, as expected from the resonance structure shown, the positive charge (Mulliken charge) on the hydrogen of the methyl changed as the methyl rotated. It had a minimum value when the torsion angle was 0° (+0.121), increased to a maximum (+0.133) at a torsion angle of 72°, then reduced to a minimum (+0.119) and 162°, and went to a small maximum (+0.120) at 180°. The bond order of the C—H bond cannot

be conveniently retrieved from our printouts, but it is clear from the bond length changes that it is a maximum near 0 and 180° and a minimum near 90°.

Thus there is no question about the hyperconjugative effect in the *ab initio* calculation. It is clear and unambiguous. Since the maximum amount of stretching in a properly oriented C—C bond in an alkene is only 0.006 Å from our formulation, it might be thought that this effect is small enough to ignore, and indeed it is questionably beyond experimental error. But sometimes several double

**TABLE I.**  
**Compounds showing long C—C bonds (Å).**

Compound	Bond	Expt. <sup>6-9</sup>	MM4 <sup>e</sup> / Δ	MM4 <sup>f</sup> / Δ	Hyperconj. Effect
1	C5—C13 <sup>h</sup>	1.621(2) <sup>a</sup>	1.603 / - 0.018	1.618 / - 0.003	0.015
2	C13—C14	1.571	1.565 / - 0.006	1.574 / 0.003	0.009
3	C1—C7 <sup>h</sup>	1.617(5) <sup>a,b</sup>	1.589 / - 0.028	1.623 / 0.006	0.034
4	C1—C7	1.623(3) <sup>a,b</sup>	1.585 / - 0.038	1.613 / - 0.010	0.028
5	C1—C2	1.649(3) <sup>a,b</sup>	1.594 / - 0.055	1.616 / - 0.033	0.022
	C3—C4	1.556(3) <sup>a,b</sup>	1.542 / - 0.014	1.549 / - 0.007	0.007
6	C1—C2 <sup>h</sup>	1.570(2) <sup>a,b</sup>	1.572 / 0.002	1.572 / 0.002	0.000
	C1—C10	1.606(2) <sup>a,b</sup>	1.591 / - 0.015	1.594 / - 0.012	0.003
7	C1—C2	1.554 <sup>a,b</sup>	1.567 / 0.013	1.569 / 0.015	0.002
	C—C5	1.582 <sup>a,b</sup>	1.573 / - 0.009	1.572 / - 0.010	-0.001
	C1—C10	1.544 <sup>a,b</sup>	1.543 / - 0.001	1.544 / 0.0	0.001
	C2—C9	1.624 <sup>a,b</sup>	1.586 / —	1.592 / —	0.006
	C5—C6	1.585 <sup>a,b</sup>	1.578 / - 0.007	1.583 / - 0.002	0.005
	C6—C11	1.556 <sup>a,b</sup>	1.555 / - 0.001	1.556 / 0.0	0.001
	C9—C10	1.570 <sup>a,b</sup>	1.568 / - 0.002	1.569 / - 0.001	0.001
	C11—C12	1.555 <sup>a,b</sup>	1.543 / - 0.012	1.543 / - 0.012	0.000
8	C4—C5	1.578 <sup>a,b</sup>	1.566 / - 0.012	1.567 / - 0.011	0.001
	C5—C6	1.645(8) <sup>a,b</sup>	1.628 / - 0.017	1.648 / 0.003	0.020
9	C1—C7	1.61(2) <sup>c</sup>	1.584 / —	1.613 / —	0.029
10	C1—C7	1.61(2) <sup>c</sup>	1.591 / —	1.623 / —	0.032
11	C1—C2	1.77 <sup>c,d</sup>	1.582 / —	1.604 / —	0.022
	C1—C3	1.50 <sup>c</sup>	1.555 / —	1.554 / —	-0.001
12	C1—C2	1.67(3)	1.700 / —	1.799 / —	0.009
13	C1—C23 <sup>h</sup>	~ 1.57 <sup>i</sup>	1.544 / —	1.562 / —	0.018
	AVE		-0.019 <sup>g</sup>	-0.003 <sup>g</sup>	
	RMS		0.025 <sup>g</sup>	0.012 <sup>g</sup>	

X-ray values are corrected to  $r_g$  values.

<sup>a</sup> 0.002 Å is added for the  $r_\alpha \rightarrow r_g$  correction.

<sup>b</sup> 0.005 Å is added for the thermal libration.

<sup>c</sup> Compounds 9–13 are excluded from statistical calculations, as is the C2—C9 bond in compound 7.

<sup>d</sup> See ref. 8.

<sup>e</sup> Hyperconjugative effect excluded.

<sup>f</sup> Hyperconjugative effect included.

<sup>g</sup> Bonds to which hyperconjugation contributions 0.001 Å or less are omitted in calculating the statistical comparisons.

<sup>h</sup> Several compounds in this table are not hydrocarbons, and parameters for the functional groups are not yet available for MM4. The corresponding MM3 parameters were used here. It is not expected that this approximation will make any difference in any of the results.

<sup>i</sup> J. S. Siegel, unpublished.

bonds or phenyl groups contribute to the stretching of a particular bond, so much larger stretching effects may be anticipated in such special cases. The magnitude of the numbers involved shows why it has been difficult to detect this effect experimentally in the past. The effect is small. The difference between the C—C and C—H effects is even smaller. One needs some kind of standard relative to which these small effects can be measured. The latter is not a problem with *ab initio* calculations, but for comparisons of experimental bond lengths, what is to be used as the standard in

the case when there is no hyperconjugation? Clearly, the use of molecular mechanics is indicated here. If we have a reliable calculation of a bond length by molecular mechanics (in which hyperconjugation is not included but everything else is), then any deviation of the bond length from the experimental value (apart from experimental/calculational errors) is indicative of hyperconjugation (or some other unknown effect).

There are eight compounds that have been previously considered in the literature<sup>6</sup> to have long bonds from the effect mentioned. These are shown

as compounds 1–5 and 9–11 in Figure 1. Three additional compounds may be added to the list (6–8, Fig. 1). The experimental data in the case of compounds 9–11 are less accurate than those for 1–8, so compounds 9–11 will not be discussed in detail. For compounds 1–8, relatively good quality X-ray structures are available, but they are determined at room temperature. Since the thermal motions of molecules in crystals at room temperature have significant effects on the apparent lengths of bonds, one would prefer to have low-temperature X-ray data. Such data do not exist for these compounds, although for one (compound 2), rigid-body motion corrections to the bond lengths were applied. Compounds 3–8 were therefore approximately corrected for thermal motions in the present work by adding 0.005 Å to their experimental (room temperature) bond lengths, plus a correction to convert  $r_\alpha$  to  $r_g$  (0.002 Å for C—C bonds). The data are summarized in Table I. The experimental values (corrected to  $r_g$ ) are compared with the values calculated by MM4 (for which hyperconjugation is not included). Since we desired experimental structures that were as accurate as possible to which to fit the MM4 data, we chose compound 1 to restudy. A structure at room temperature has previously been reported.<sup>6</sup> Since the crystals were still available, it was decided to restudy the structure at a much lower temperature (–120 °C) in order to minimize thermal motions and determine the bond lengths as accurately as possible, and this was done in the present work. The data given for compound 1 in Table I were from this low-temperature X-ray study.

## Discussion

For the bonds listed in Table I, the experimental bond lengths tend to be longer than those calculated by MM4 when hyperconjugation was excluded (column 3;  $\text{MM4}^e/\Delta$ ). The errors in the MM4 values are shown in the same column, where a negative value for  $\Delta$  means that the MM4 values are too short. For compounds 1 and 2, for which we believe the experimental data are most accurate, the calculated values are too short by 0.018 and 0.006 Å, respectively. For these two compounds, experimental errors expected are on the order of 0.005 Å (2–3 estimated standard deviations). So agreement to approximately this amount between calculations and experiment would be

regarded as satisfactory. Compounds 3–8 have experimental values that are somewhat less accurate. If we look at a comparison of the experimental results and the MM4 calculations in Table I for compounds 1–8, we note an average (signed) discrepancy of –0.019 Å and a root mean square discrepancy of 0.025 Å. The minus sign in the average discrepancy is particularly significant, because it means that the bonds are systematically calculated to be too short, on the average by the fairly large amount of 0.019 Å after all corrections have been applied. While occasional errors of this magnitude are not completely unexpected in crystallographic data, an error of this magnitude in the average bond length is indeed very large. MM4 will usually calculate C—C bond lengths to within about 0.004 Å, and if the experimental error is taken as 0.005 Å for compounds 1 and 2, and perhaps 0.010 Å for 3–8, a discrepancy of more than –0.018 Å for compound 1 and an average discrepancy of –0.019 Å overall suggests that there is a significant defect in the calculations for this particular group of molecules.<sup>††</sup> These bonds, all of which are more or less perpendicular to double bonds or phenyl rings, are systematically calculated to be too short. These errors are far larger than we would normally anticipate for MM4. Accordingly, we concluded that something was left out of the preliminary original version of MM4, namely hyperconjugation (see footnote || on p. 749).<sup>10</sup>

Compound 1 is a rather good compound for the present study, because there are four different phenyl groups in the molecule, each of which is contributing to the stretching of the central (5–13) bond. Since they are oriented with varying dihedral angles, the phenyls exert varying amounts of stretching, totaling to 0.015 Å (Table I) with MM4, as described earlier. This bond is also lengthened by steric effects, but that lengthening is already taken into account by MM4. The bonds in the other compounds in Table I are hyperconjugatively lengthened by various amounts as shown, from 0.000 up to 0.34 Å, depending on how many pi-orbitals contribute to the lengthening and their dihedral angles relative to the lengthened bond. The hyperconjugative effect for alkenes was therefore added to MM4 (and is included in the calcula-

<sup>††</sup> Crystal packing forces can lead to changes in bond lengths, but earlier studies (ref. 2) have shown that these almost always lead to compression of the bond and that changes as large as 0.002 Å are infrequent.

tions reported in earlier articles<sup>9</sup> with the formulation indicated).

When this hyperconjugative effect from the unsaturated system on the  $\sigma$  bonds of the molecule is taken into account, the results obtained are as shown in Table I for MM4 (column 4). Note that the overall systematic error has been reduced markedly for the compounds weighted in Table I, from  $-0.019$  Å to  $-0.003$  Å. The root mean square error is similarly reduced, from  $0.025$  Å down to  $0.012$  Å, and these reduced errors are in the range anticipated for the experimental/calculational error. The parameters derived for the hyperconjugative effect are listed in Table II.

Our conclusions are that the hyperconjugative effect of unsaturated groups on C—C bonds is real beyond doubt, both by *ab initio* calculation and by X-ray crystallography, and that it leads in some cases to bond length stretchings as large as  $0.034$  Å, as shown by the several molecules listed in Table I. It was shown earlier that the hyperconjugative effect on bond lengthening from a C=O group is much larger than from a C=C group, and it seems clear that any unsaturated group will have a qualitatively similar effect. Hence any molecular mechanics scheme that attempts to calculate bond lengths in general with an accuracy of greater than about  $0.034$  Å will have to explicitly take this effect into account, and this has been done with MM4. This effect is calculated to be of a similar magnitude with MM3, and it has also been

included in MM3(94) and will be included in later versions of these programs.

## EXPERIMENTAL

The crystal growth and room temperature structure of indanoindane 1 were described earlier.<sup>6</sup> For the present work, the X-ray diffraction data were measured at  $-120^\circ\text{C}$  on an Enraf-Nonius CAD4  $\kappa$ -axis diffractometer using graphite monochromated Mo radiation [ $\lambda(K\alpha) = 0.71073$  Å]. Final cell dimensions were obtained by a least-squares fit to the automatically centered settings for 25 reflections ( $2\theta > 22^\circ$ ). Periodic measurement of three standard reflections showed no intensity loss during the experiment. Intensity data were corrected for absorption and for Lorentz and polarization effects. Atomic scattering factors and mass attenuation coefficients were taken from ref. 6. The final least-squares refinement cycle (SHELX) included independent positions for all atoms, anisotropic thermal coefficients for non-H atoms, isotropic thermal coefficients for H atoms, and an empirical extinction parameter. The final differ-

**TABLE II.**  
Parameters for Hyperconjugation [Eq. (2)] in MM4.<sup>a</sup>

	$K_{V1}$	$K_{V2}$
1-1-2-2	0.000	0.116
1-1-2-112	0.150	0.216
1-1-122-112	0.150	0.216
1-1-122-122	0.000	0.116
123-123-2-2	0.000	0.116
123-123-122-122	0.000	0.116
123-123-122-112	0.150	0.216
56-56-2-2	0.000	0.116
56-56-122-112	0.150	0.216
56-56-122-122	0.000	0.116

<sup>a</sup> Atom types are as follows:  $\text{sp}^3$  carbon 1, in a 5-membered ring 123, in a 4-membered ring 56;  $\text{sp}^2$  carbon 2, in a 5-membered ring 122. Hydrogen attached to  $\text{sp}^2$  carbon is Type 112.

**TABLE III.**  
Low-Temperature Crystal Data for Indanoindane 1.

Formula	$\text{C}_{31}\text{H}_{27}\text{NO}_5$
Crystal system	Triclinic
Space group	$P\bar{1}$
$a$ , Å	10.690(3)
$b$ , Å	12.313(4)
$c$ , Å	10.453(5)
$\alpha$ , deg.	94.87(4)
$\beta$ , deg.	106.44(3)
$\gamma$ , deg.	109.48(3)
$V$ , Å <sup>3</sup>	1219(2)
$Z$	2
Temp. $^\circ\text{C}$	$-120$
Density, calcd., $\text{g}/\text{cm}^3$	1.344
Crystallizing solvent	Methanol
Crystal habit	Tabular (yellow)
Cryst. dims., mm	$0.10 \times 0.52 \times 0.60$
$\mu$ , $\text{cm}^{-1}$	0.85
Transmission factor range	$0.991 - 0.953$
Extinction factor	$4.0(5) \times 10^{-7}$
$2\theta$ limit, deg. (octants)	$48 (\pm h \pm k - 1)$
Intensities (unique, $R_i$ )	4281 (3822, 0.013)
Intensities $> 2.58\sigma(I)$	3062
$R$	0.030
$R_w$ [for $w = 2.37 / \sigma^2(F_o) + pF_o^2$ ]	$0.032 (p = .01)$

ence Fourier map had no significant features, and a final analysis of variance between observed and calculated structure factors showed no systematic errors. Pertinent information is given in Table III and in the Supplementary Material.

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## Conclusion

This article, together with the four preceding articles, constitutes the development of an experimentally based (mostly) force field for saturated hydrocarbons, alkenes, and conjugated polyene systems. The overall capabilities of the force field are similar to, but somewhat better than, those of the earlier program. MM3.

Also printed in this issue of the *Journal of Computational Chemistry* are five articles by T. A. Halgren, in which he discusses a force field derived by *ab initio* methods on which we may briefly comment. *Ab initio* methods are certainly competitive now with experimental methods for determining structures and properties of molecules, and particularly for constructing force fields. Sometimes the experiments can be done more accurately, but often there are various kinds of errors that creep into the experiments, so it is most desirable to compare both the calculated and the experimental values insofar as this can be done.

The objectives of Halgren in developing his force field were different from our own objectives, and the two force fields are consequently not comparable. Nevertheless, they tend to give rather similar results for many problems. What we have published here concerns only hydrocarbons, although we have done considerable work on functionalized molecules and will publish that in due course. In general, our force field is more highly refined than Halgren's in the sense that it contains many more kinds of terms and accounts for things like electronegativity and hyperconjugation. His general approach has been to optimize all kinds of compounds at the same time, whereas we have used the functional group approach. The advantage of the former method is that a saturated carbon-carbon bond, for example, gets the same treatment in every different kind of molecule. Hence if one is trying to reproduce structures of molecules in general, that is in principle a better way to do it. The advantage of the functional group method is that different functional groups can have pronounced effects on various things, such as carbon-carbon bonds. When everything is

optimized together, one does not necessarily observe this effect. But if one optimizes the hydrocarbons first, then the presence of, for example, an electronegative substituent leads to severe bond shortenings which are readily detected, and then one can add appropriate terms into the force field to compensate for this. So in our view, the latter approach may be better at uncovering unforeseen effects.

Since *ab initio* methods are so powerful now, one may ask why carry out molecular mechanics calculations anyway? The answer is that for large systems, such as proteins in aqueous solvent, one is not likely to want to do *ab initio* calculations anytime soon. In general, the expedient way to go would seem to be to use *ab initio* calculations to develop force fields and then use force fields to do the real calculations on molecules. As the accuracy of the *ab initio* calculations increases, the reliance on experimental measurements will correspondingly decrease.

But molecular mechanics can teach us things about molecules that are difficult to learn from *ab initio* calculations directly. This article is an illustration of this fact. We have a model of molecules (molecular mechanics), and we calculate molecular properties. If we get a systematically wrong answer, it means something has been left out of our model (in the present case, hyperconjugation). We can develop a way to treat hyperconjugation, or presumably anything else, and build this into our mechanical model. When that is properly done, the model faithfully reproduces the properties of the molecules. We not only get good numbers, but we also gain an understanding of what is going on.

One of the nice features of the early molecular mechanics models was that they were very simple (class 1 force fields, harmonic and diagonal). Might one reasonably suppose that as one adds more and more complications to the model one will lose sight of what is really going on? The Hückel MO calculation, for example, is a simple picture that gives us a great deal of insight. However, for numerical calculations, it is not very useful. A similar thing is true in molecular mechanics. A class 1 force field gives us a lot of insight, but is not very useful for calculations. Fortunately, as we add additional terms in going to a class 2, and then to a class 3, force field, it is usually still easy to see what is going on. In looking at the results for a particular molecule, the consequences of bending, stretching, etc. are just as clear as they were previously, but when things like stretch-bend interactions or bend-torsion-bend interactions oc-



cur, looking at the appropriate data also makes it clear just what they are doing.

One might wish that nature had made molecules more simple so that the class 1 force field gave numerically accurate results. However, nature chose not to do this. Accordingly, if we want to understand what nature has done, and have a reliable calculational method for interpreting this and for predicting cases that we do not yet know about, then we need a more complicated force field. This is, of course, not ours to choose, but just the way it is.

### Supplementary Material

Tables listing positional parameters and anisotropic thermal factors for indanoindane are available from the authors upon request. The package of Supplementary Material referred to in the text (X-ray positional and thermal parameters, three pages) is available from the authors upon request.

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